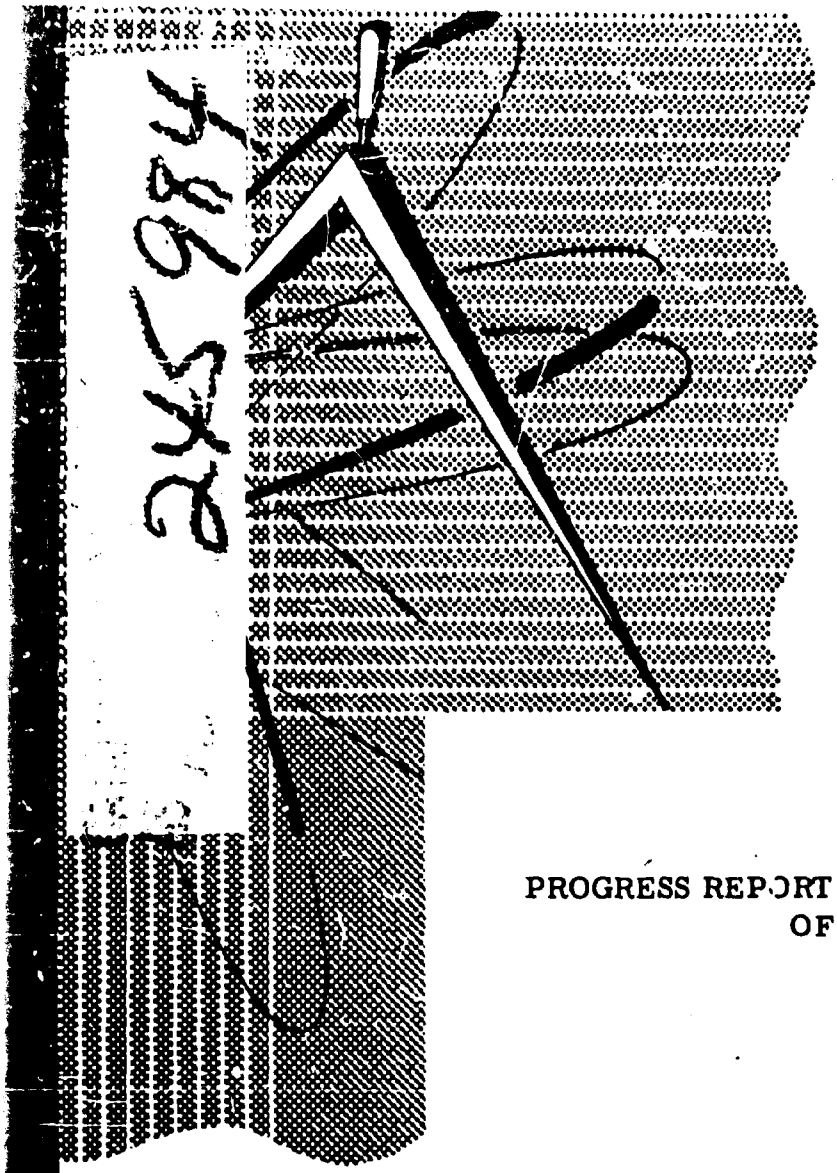

NDA 2118-1

PROGRESS REPORT ON DISSOLUTION AND SOLUBILITY OF METALS IN LITHIUM

B. Minushkin
H. Steinmetz

March 31, 1960

Work Performed on Contract Nonr-2857(00)
for the Office of Naval Research

NUCLEAR DEVELOPMENT CORPORATION OF AMERICA
WHITE PLAINS, NEW YORK

NDA 2118-1

PROGRESS REPORT ON DISSOLUTION AND SOLUBILITY OF METALS IN LITHIUM

B. Minushkin
H. Steinmetz

March 31, 1960

Work Performed on Contract Nonr-2857(00)
for the Office of Naval Research

NUCLEAR DEVELOPMENT CORPORATION OF AMERICA
White Plains, New York

CONTENTS

TABLES

FIGURES

1. SUMMARY

This paper is a report of the initial phase of an investigation of the kinetics of dissolution and the solubility of structural metals in lithium. The theoretical background and considerations leading to the choice of experimental methods are presented.

Activity to date has been concerned primarily with selection of methods, development of experimental techniques, procurement, construction, and installation of equipment. Shakedown tests on the equipment and experimental techniques were performed. Several subsidiary problems associated with the development of the experimental techniques were investigated.

2. INTRODUCTION

Corrosion of many structural metals by lithium generally results in mass transfer of metal through a thermal gradient. The mass transfer process involves dissolution of the container metal at the hot end, transport of the dissolved metal by flowing liquid to the cold end, and deposition of the excess solute at the cold end. The process is believed to be of the "solution type"[1,2,3] and therefore the ultimate factors governing the rate of attack are the kinetics of dissolution and the solubility relationship for the solid metal in lithium.

A summary of the classified and unclassified literature, to 1959, on containment of lithium is given by Hoffman.[4,5] The work reported has been developmental and concerned primarily with the containment of lithium in engineering systems. There is little information on the kinetic and solubility relationships for metals dissolving in lithium; in particular it is unknown whether the rate controlling step during dissolution is a transport or chemical process.

This paper is a report of the initial phase of an investigation of the kinetics of dissolution and the solubility of structural metals in lithium. The program is limited to a study of two component systems (lithium plus pure metal) under isothermal conditions. The effects of temperature, agitation, and lithium purity are being investigated in order to establish the detailed mechanism of the dissolution process.

3. PROGRESS TO DATE

Activity to date has been concerned primarily with selection of methods, development of experimental techniques, procurement of materials and design, construction, installation, and shakedown of equipment. These activities are presented in Section 5 and the Appendixes.

The equipment required for this investigation has been designed, built, and operated. Techniques for stirring and sampling lithium at test temperatures, without introducing contamination, have been developed and used in preliminary tests. A method of following the dissolution process of iron using iron-59 tracer has been applied. A vacuum distillation purification system (used previously at NDA)[13] has been put into operation to insure a supply of uniformly pure lithium.

Several subsidiary problems associated with the development of the experimental techniques were also investigated. These included methods of producing thick, uniform, and adherent electroplated layers of iron (containing Fe^{59}) on the Armco iron liner and stirrer, and investigation of the possible effects upon specific activity of interdiffusion between iron of the plated layer and the base metal.*

Some preliminary tests on the solution rate of iron in lithium at 1400°F with and without stirring were performed. These were intended primarily to test the apparatus and operating procedures. However, the results are presented and discussed in Section 5.3. Although much more work is required to provide the desired information on kinetic and solubility relationships for iron in lithium, the work done so far has made us confident that the apparatus and techniques which have been developed will prove capable of providing this information.

*See Appendix III.

4. THEORETICAL BACKGROUND

A theoretical treatment of the kinetics of dissolution of solids in liquids is presented by Moelwyn-Hughes.[6] This theory has been formulated from studies of the dissolution of organic and inorganic salts in water and in other solvents. However, in recent years this same theory has been applied to the study of the kinetics of dissolution of metals in liquid metals.[7-12]

According to the Nernst-Brunner theory, the dissolution process is composed of two steps. The first is a surface reaction in which solute atoms cross the solid-liquid interface into the liquid phase. The second step is the diffusion of solute atoms from the interface through a liquid boundary film (which is presumed to exist at the interface) into the bulk liquid phase. The net rate of dissolution will be determined by the slower of the two steps. When the surface reaction rate is rapid with respect to the diffusion rate, the boundary film becomes saturated and the solution process is "diffusion limited." When the reverse situation occurs, i.e., the surface reaction rate is slow with respect to the diffusion rate, the boundary layer is not saturated (or nonexistent) and the process is "solution-rate limited."

Formal development[6] of this theory yields the following expressions for the rate of solution:

$$dS/dt = \alpha\left(\frac{A}{V}\right)\ (S^0-S)$$

or

$$S = S^0\left[1-\exp\ \left(-\frac{\alpha At}{V}\right)\right]$$

where S = concentration of solute at time t
S^0 = concentration of solute at saturation
t = time
A = area of dissolving solid
V = volume of liquid
α = solution rate constant.

From these equations it is seen that for a given system at constant temperature the dissolution process is characterized by the solution rate constant, α. The solution rate constant is related to the rate determining step. When the surface reaction is the slower of the two steps, the constant is equal to a chemical rate factor,

$$\alpha = k_S.$$

The solution rate constant will be related to a frequency factor,[6] will exhibit a characteristic temperature dependence, and will probably be sensitive to purity.

When diffusion is the slower of the two steps, the solution rate constant is given by:

$$\alpha = D/\Delta$$

where D is a diffusion constant for the solute in the liquid and Δ is the thickness of the boundary film. The solution rate constant will be proportional to the relative velocity of movement of the solute and the solvent and to the viscosity of the fluid as shown by Ward and Taylor.[8] The dissolution rates will be given by the equation for diffusion of solute atoms across a liquid film of thickness Δ.

This theory has been used successfully by a number of investigators in analyzing the kinetics of solid metal-liquid metal solution processes. Ward and Taylor[7,8,9] studied the kinetics of dissolution of copper in liquid lead and bismuth and of iron in liquid bismuth. By measuring the solute concentration as a function of time at a number of temperatures and under static and dynamic conditions, they concluded that the net rate of dissolution was determined by the diffusion step. Similarly, Bennett and Lewis[10] concluded that the rate of dissolution of lead and tin in mercury was "diffusion limited" while the rate of dissolution of zinc in mercury was "solution-rate limited." Lommel and Chalmers,[11] employing a somewhat different experimental technique, concluded that the dissolution of lead in liquid lead-tin alloys was diffusion limited when there was no stirring, while at high stirring rates it was solution-rate limited.

Epstein,[12] using data from nonisothermal mass transfer loops, showed that dissolution of iron in liquid sodium appeared to be solution-rate limited and that the reaction rate was to a first approximation proportional to the oxygen content of the sodium. It is commonly observed that for cases where dissolution is not diffusion limited it is possible to find a chemical reaction occurring at the solid-liquid interface which controls the dissolution rate. This is an important consideration in lithium systems where experience indicates that nitrogen and possibly other chemical impurities accelerate corrosive attack.

5. EXPERIMENTAL

In view of the successful application of the Nernst-Brunner theory to dissolution studies in other liquid metal systems, the dissolution of metals in lithium is being investigated within the framework of this theory. Accordingly, an experiment was planned to measure the solution rate constant and solubility of metals in lithium.

The simplest system that can be studied is one in which a pure metal (solute) is dissolved into a pure liquid metal, there being no terminal solid solubility nor intermetallic compounds in the phase diagram between the two metals, and only slight solubility of the solid in the liquid metal. Such a system is formed between lithium (and indeed most other common liquid metals) and iron or nickel for example.

Iron was chosen for this phase of the study because it is easily available in pure form and is easy to handle. In addition, it is believed to behave in lithium in a manner similar to other interesting metals and alloys of more immediate applicability which are either too difficult to handle or too complex to consider in this stage of the investigation.

5.1 SELECTION OF METHOD

The solution-rate constant and saturation solubility are generally obtained by measuring the solute concentration in the liquid as a function of time of contact. The saturation solubility is then the asymptotic value of the S vs t curve. The solution rate constant is obtained as the slope of a plot of $\ln(S^0-S)$ vs t. The influence of temperature lithium purity, and rate of stirring upon the solution rate constant and of the former two upon the saturation solubility will provide the information required to establish the mechanism of the dissolution process.

Two alternative procedures are possible. In the first, a large volume of liquid metal is employed, from which small samples are withdrawn during the course of dissolution and analyzed for dissolved metal. In the second procedure, a number of much smaller volumes of liquid are brought into contact with solid and each subsequently analyzed for dissolved metal. The latter method has the advantage of avoiding sampling errors, since the entire volume is taken for analysis. However, this method would tend to strain the reproducibility of the apparatus and procedures. In addition, the required apparatus poses a number of design and manipulative problems. Based upon these considerations and its successful use in earlier investigations,[3] the former method was adopted.

Although suitable chemical techniques for determining microgram quantities of iron are available, these methods are relatively cumbersome and time consuming. Radioactive tracer techniques appear to be ideally suited to follow the dissolution process. They are fast, sensitive, and specific. The use of iron-59 with its penetrating 1.10 and 1.29 Mev gamma permits determination of sample activity without the necessity for removing the lithium sample from its container. For these reasons tracer techniques using iron-59 were developed to measure the solute concentration during the dissolution experiments.

5.2 APPARATUS AND PROCEDURES

The apparatus which was designed and built to measure the solution rate constants and solubility of metals in lithium is shown in Figs. 1 and 2. It consists of a stainless steel vessel with an inner liner of the metal under investigation (iron at present) for containing the lithium, and a concentric cylindrical stirrer made of the same material as the liner. The stirrer is driven by a variable speed motor operating through a magnetic coupling to minimize contamination which would be introduced by seals. The vessel is sealed by a rubber O-ring and cover plate. Attached to the cover plate are a thermocouple well, radiation shields, magnetically coupled stirrer shaft housing, and two gas locks. Lithium is introduced into the vessel through a heated line which passes through one of the gas locks during the filling operation. Samples of lithium are removed during the course of dissolution, without exposing the lithium to atmospheric contamination, by means of sampling tubes which pass through Wilson seals on the gas locks.

The bottom section of the retort is heated by an electric furnace which is controlled by a chromel-alumel thermocouple attached to the vessel wall. The thermocouple actuates a Minneapolis-Honeywell Pyro-Vane controller. A second thermocouple is located in the well which dips into the lithium to measure and record its temperature. With this system, the lithium temperature is maintained within ±4 °F. Temperature traverses in the thermocouple well showed no detectable vertical gradients from the bottom of the liner to within a small fraction of an inch of the lithium surface.

Associated with the retort are a gas and vacuum manifold and the lithium fill and drain system. The vacuum system is used for outgassing the retort and gas lock prior to each test. Helium is used as a cover gas during the test; by adjustment of pressures it is used to transfer lithium into and out of the retort. All lines, valves, and vessels which carry lithium have provisions for electrical heating to a temperature above the melting point of lithium.

The procedure which has been tentatively adopted is as follows: a 0.002-in. thick layer of iron containing a known quantity of iron-59 tracer is electroplated from a chloride bath onto the Armco iron liner and stirrer.* The apparatus is assembled and the plated liner and stirrer are annealed in flowing dry hydrogen (dew point: -90 °C) for 1 hr at 1700 °F. They are allowed to cool under hydrogen to about 800 °F and then vacuum outgassed at less than 1 micron for about 2 hr. The vessel is then preheated to the test temperature and a measured quantity of vacuum distilled lithium[13] is transferred into the iron liner. Samples of the lithium are collected prior to the transfer, as soon as the lithium reaches the desired test temperature and periodically thereafter. Lithium samples were collected in 1/2 in. diameter by 3-in. long stainless steel tubes. It was desired to collect 1 gram samples; however this proved difficult to control and the sample sizes varied from 0.3 to 2.9 grams.

A well-type Thallium activated NaI scintillation detector and single-channel pulse height analyzer was used to determine the iron activity of the lithium samples.† The sample tube, in a rubber finger cot to protect the detector, was placed in the well of the crystal and counted at the 1.1 Mev gamma peak. Counting rates were very low (in most cases), and 1-hr counts were taken. The lithium was dissolved out of the container and the quantity of lithium determined by titration with standard acid.

Samples were also taken of the plating solution at the end of the plating. These samples were diluted and 2 cc portions of the diluted solutions placed into glass vials which were put into the well, counted, and then analyzed for total iron.

---

* See Appendix I for details of the plating procedures.

† See Appendix II for details of counting and analytical techniques.

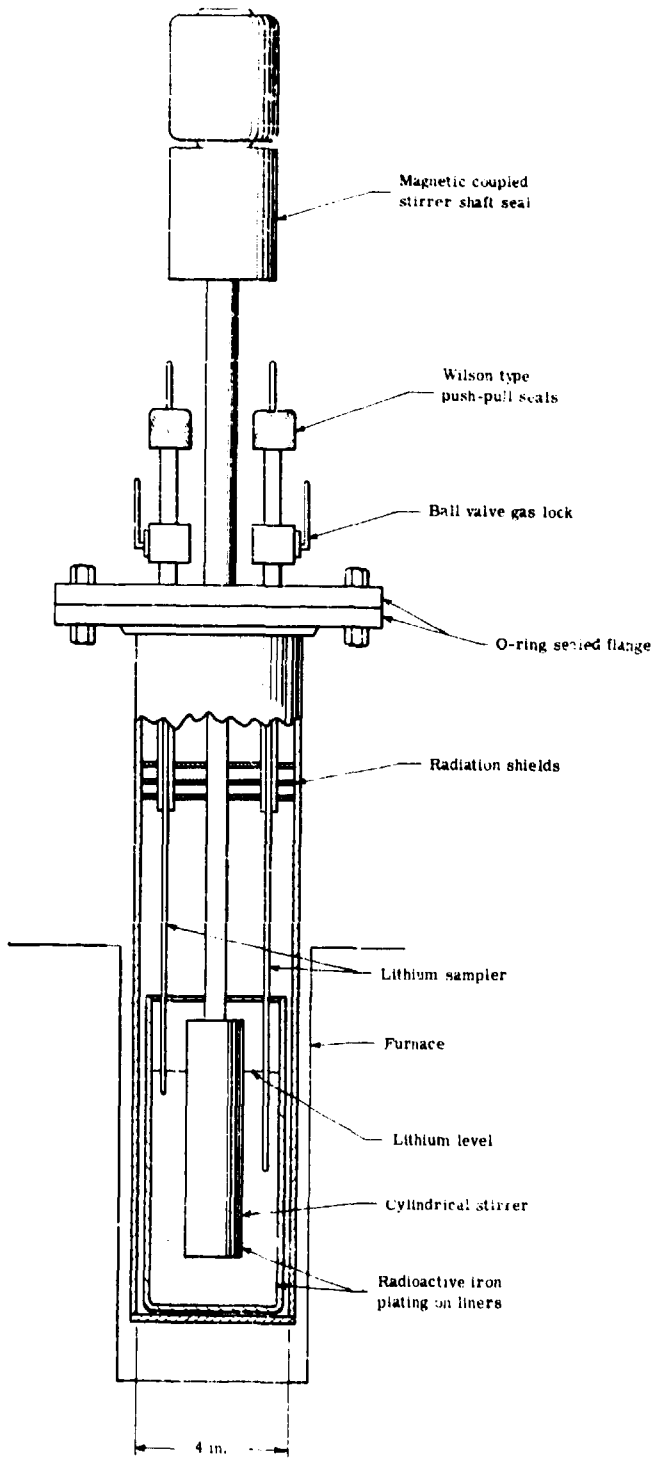

Fig. 1 — Solution rate and solubility apparatus – schematic

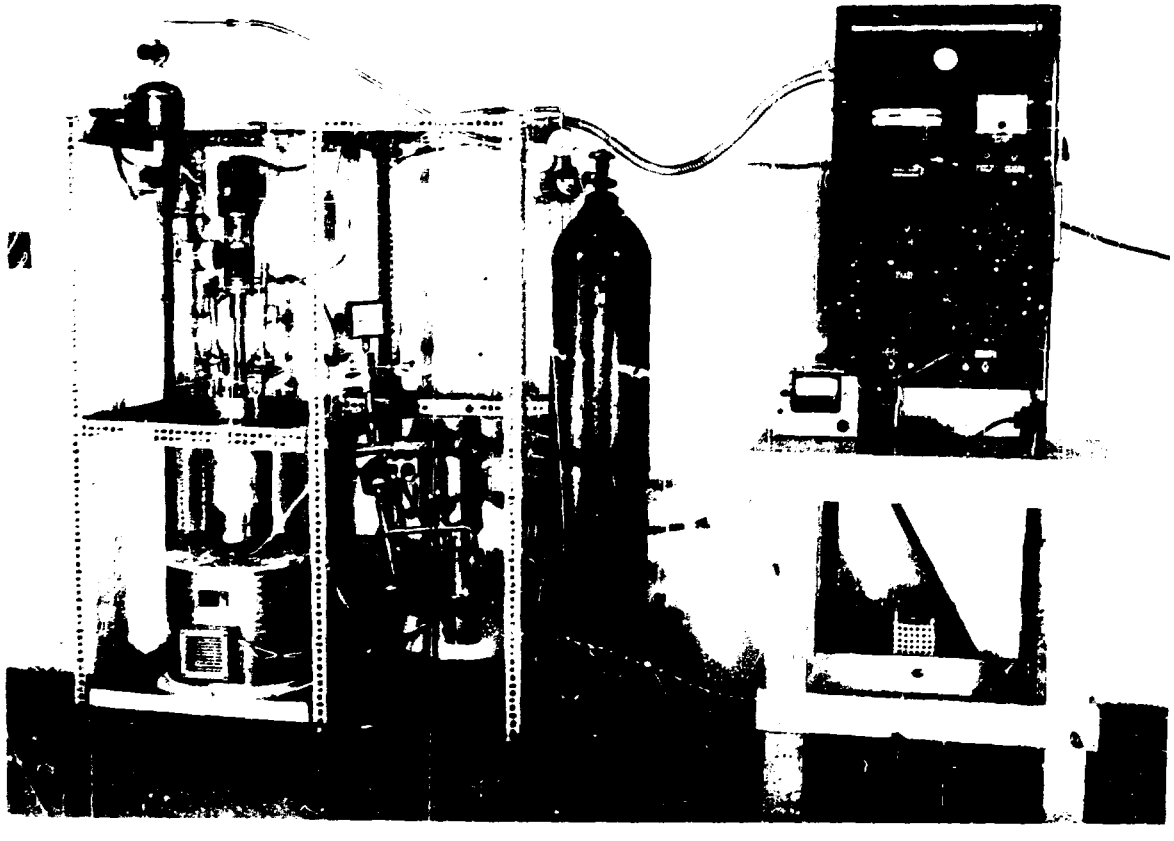

Fig. 2 — General view of apparatus for measurement of solution rate and solubility

Swipe samples were taken of the stirrer and liner at the end of the run. A piece of filter paper soaked with 6M HCl was wiped across the plated surface. Some of the plated iron was dissolved and adhered to the filter paper. The filter paper was then decomposed with acid and the resulting solution counted and analyzed for total iron.

These two measurements of the specific activity (which did not differ by more than 15%) were used to relate the sample count rate to the total iron content.

5.3 RESULTS OF FIRST RUNS

The first run did not utilize iron-59 tracer. Therefore, no solution rate data were obtained. The second run (see Table 1) was made at 1400°F following the procedure outlined in Section 5.2. During the first 4 hr, the lithium was nominally static. After 4 hr, the stirrer was rotated at 260 rpm (2.3 ft/sec peripheral velocity).

The data provide an indication of the magnitude of the solution rates and solubility values, and outline problem areas for planning future work. The data exhibit the expected trend, i.e. increasing concentration with time, and what appears to be a significant increase in solution rates after the start of stirring. Saturation seems to have occurred sometime after the fourth hour. However, because of the scatter, neither the time for saturation nor the value of saturation solubility can be deduced. Agreement between the radiochemical and colorimetric determination of iron content (sample 27.5 hr) appears satisfactory. (This is also true of other samples which were analyzed by both methods.)

The following possible causes of scatter in the solute concentration data are obvious and steps will be taken to eliminate them.

1. The low level of activity used in the preliminary experiments resulted in rather poor counting statistics and errors of up to ±25% in the solute concentrations. Future experiments will be conducted at substantially higher activity levels to remove this source of error.
2. Counting efficiency may have varied by up to 50% as a result of variations in sample size and geometry. A new type of sampling bucket will be used which will limit sample size to 1 gram (2 cc). In addition, the use of a larger well-type scintillation detector will substantially improve the overall counting efficiency.

Additional work is planned to ascertain and eliminate these and other sources of error and determine the reproducibility of the experimental measurements.

Table 1 — Results of Run 2

Temperature: 1400°F; Surface Activity: 0.85 counts/min-μg Fe;
Nitrogen Content of Lithium: 250 ppm

Time, hr	Counts Above Background	Weight of Li, g	Concentration of Fe, ppm		Stirrer Condition
			Radiochemical	Colorimetric	
0	6 ? ± 1.5	2.62	2.8		Static
0.25	17.9 ± 1.5	2.82	7.5		Static
0.50	9.6 ± 1.5	0.47	24.3		Static
1.0	11.8 ± 1.5	2.44	5.8		Static
2.0	14.7 ± 1.5	1.67	10.2		Static
4.0	11.8 ± 1.5	0.99	14.0		Static
5.5	33.2 ± 1.6	1.00	39.1		Stirred at 260 rpm
8.0	17.8 ± 1.5	0.30	70.0		Stirred at 260 rpm
12.0	23.5 ± 1.6	1.41	19.2		Stirred at 260 rpm
24.0	59.9 ± 1.8	1.29	54.5		Stirred at 260 rpm
27.5	26.4 ± 1.6	0.78	40.0	35	Stirred at 260 rpm
29.5	45.5 ± 1.7	2.19	24.5	29	Stirred at 260 rpm

APPENDIX I

Plating Technique

One method of preparing the radioactive liner and stirrer for the lithium is to irradiate inactive iron parts with the neutron flux of a reactor. Using this method, a rather large mass of iron would be activated. The total iron activity handled in these experiments would be large, accordingly. In addition, if the cobalt content of the irradiated container is greater than 1 ppm, there would be an appreciable interference due to Co^{60} activity.

For these reasons it was proposed that an inactive iron liner and stirrer be electroplated with radioactive iron. The optimum procedure for electroplating iron activity onto an iron liner and stirrer was determined in a number of preliminary experiments.

The first experiments involved the electroplating of iron onto 1 in. × 8 in. sections of Swedish iron foil. The weight gain was noted and in a few cases the plating thickness was measured. The plates were also examined for the presence of pits, graininess and brittleness.

On the basis of these small-scale tests, several methods were further tested at full scale. An Armco iron liner 8 in. tall with an ID of $3\frac{3}{4}$ in. was filled with plating solution. The liner was made the cathode. After the electroplating was completed, the plate was examined for uniformity, smoothness of surface, and freedom from pitting.

Carbonate Bath

A procedure for plating iron from a concentrated solution of ammonium carbonate was reported by Armistead.[14] This method is attractive because the plating solution can be electrolyzed until the iron in solution is completely plated out. Therefore, in plating radioactive iron the amount of activity handled would not be greater than the amount plated.

In the small scale tests it was found that the iron deposited from the carbonate bath to form an adherent, ductile, uniform plate with a matte surface. A serious disadvantage is that the quantity of iron that can be dissolved in the carbonate solution is very limited (2 grams of iron per liter). To prepare a moderately thick plate, it is necessary to electrolyze several portions of plating solution. It was also observed that during electrolysis a considerable amount of spray was formed. A system for collecting this spray would be necessary when plating from a radioactive solution.

In the full-scale tests, plating at a current density of 80 milliamperes/cm^2 resulted in a low rate of plating and in a nonuniform plate. It is possible that this could be improved by plating at higher current densities. However, the necessary equipment was not available and an alternate plating procedure was used.

Chloride Bath

A number of well-developed procedures for electroplating iron with solutions of ferrous

chloride or ferrous sulfate exist. The major disadvantage of these baths, for plating iron-59, is that a considerable amount of dissolved iron must be present in the plating solution (about 100 grams of iron per liter). This means that the amount of iron activity handled is several times larger than the quantity actually plated.

The procedure described in Reference 15, for plating iron from a chloride bath, was followed. The initial small-scale tests showed a considerable amount of pitting. This was eliminated by the addition of 0.1 to 0.2% of a wetting agent (Laboratory Aerosol) to the electrolyte bath. The plated iron was adherent but quite brittle. Upon annealing the plate became ductile.

In the full-scale tests, a cylinder of Armco iron was used as the anode. The deposits were very rough and dendritic. The solution appeared to contain much suspended graphite. In subsequent tests, the anode was placed inside a cotton bag. This resulted in a marked improvement in the quality of the iron plate. The plate was quite smooth and had relatively few pits. Separate tests showed that, for the conditions used in electroplating, the cathode efficiency was 90%.

The following procedure was used to plate iron-59 onto the liner and stirrer. The plating solution was prepared by dissolving 740 grams of $FeCl_2 \cdot 4H_2O$ and 300 grams of $CaCl_2$ in 2 liters of water containing 2 cc of concentrated HCl. Steel wool was added to this solution, which was then set aside in a closed bottle for several hours. Before use, the solution was filtered, 2 ml of Aerosol added, and the pH adjusted to 0.0 to 0.5.

An iron liner 8 in. tall with an ID of $3\frac{3}{4}$ in. was plated on the inside, to a height of 7 in. The surface area plated was 603 cm^2 and a 0.001-in. thick iron plate would weigh 12.0 grams. The crucible was degreased with chloroform, etched with 20% nitric acid and then with 50% hydrochloric acid. The crucible was rinsed with distilled water and immediately filled with 1090 cc of plating solution.

A bagged Armco iron anode of $1\frac{1}{2}$ in. OD was then immersed in the plating solution. One ml of a solution containing iron-59 (obtained from ORNL and containing approximately 1 mc Fe^{59}/ml) was added to the plating solution. The solution was heated to 85°C and the electroplating started. During the plating, the solution was stirred vigorously. The plating period was 68 min at 22.5 amperes. This was calculated to give a 0.002-in. thick plate. The plating solution was then poured out of the crucible and the crucible washed with water and acetone.

Plating of the stirrer was done in a similar manner. A cylindrical Armco iron rotor of 2 in. diameter was plated to a height of 6 in. This corresponded to a plated surface area of 257 cm^2 and a weight of 5.11 grams of iron for a 0.001-in. thick plate. An Armco iron crucible that had previously been plated with inactive iron was used as the cathode and the container for the plating solution. The rotor was degreased and etched. It was then centered inside the crucible which contained 970 cc of plating solution. Then 0.8 cc of the ORNL iron-59 solution was added. Plating was at 12.5 amperes for 52.5 min to give a plate calculated to be 0.002 in. thick.

The handling of the radioactive solutions and the electroplating was done behind a 2-in. thick lead shield.

In order for the tracer method of determining iron concentration to have validity, it is necessary that the plated surface on the rotor and the crucible have essentially the same specific activity. A complicating factor arose from the fact that an inactive iron anode was used. The result was that the specific activity of the solution was changing continuously during the electrolysis. If the cathode and anode efficiencies are equal, this can be treated as a simple dilution problem. The expression for the specific activity is then given by

$$Z = Z_{0e}^{-w\ c}$$

where Z_0 = initial specific activity of the iron in solution
Z = specific activity of the iron in solution (or surface of plate) at the end of plating
w = weight of iron plated
c = weight of iron dissolved in solution.

For the liner plating, $Z/Z_0 = 0.81$, while for the stirrer plating $Z/Z_0 = 0.90$. By setting the initial total activity in the stirrer solution at 0.8 that of the initial total activity in the liner solution, the final specific activities are equal.

Actually, the cathode efficiency was not 100%. A considerably more complex expression results if allowance is made for this fact. However, for a cathode efficiency of 90%, the use of a more rigorous expression affects the results by only about 1%.

After the liner plating had been completed, a sample of the plating solution was retained and the specific activity of the iron in solution determined. It was found to be 0.97 ± 0.02 counts/min-μg of iron. A similar determination on the solution used in plating the rotor gave a value of 1.02 ± 0.02 counts/min-μg of iron.

Upon completion of the solution rate experiment, the specific activities of stirrer and liner surfaces were determined. A piece of filter paper soaked with 50% HCl was quickly wiped over a section of the metal surface. Some of the plated iron was dissolved and adhered to the filter paper. The filter paper was then decomposed with nitric and perchloric acid and the resulting solution counted and analyzed for iron. Three such swipes were taken of the surface of the rotor and the specific activity found to be 0.81 ± 0.03 counts/min-μg of iron. The corresponding value for the liner surface was found to be 0.85 ± 0.03.

APPENDIX II

Counting and Analytical Techniques

The counting equipment consisted of a single channel pulse height analyzer (Atomic Instrument Co. Model 510) and a well-type thallium-activated sodium iodide crystal (crystal dimensions: $1^{3}/_{4}$ in. diam. × 2 in. with a 5/8 in. diam. × $1^{1}/_{2}$ in. well). The activity used was essentially radiochemically pure iron-59. Iron-59 has a 45.1 day half-life and emits gammas with energies of 0.191, 1.098, and 1.289 Mev. The base line and channel width settings on the pulse height analyzer were adjusted so that the 1.10 Mev photopeak was counted.

Measurements of iron-59 activity were made on samples of lithium that were contained inside 1/2 in. OD × 3 in. stainless steel tubes. These tubes were placed in the well of the scintillation crystal and counted for 1-hr periods. The necessary decay and background corrections were made. The lithium was then dissolved out of the container and the quantity of lithium determined by titration with standard acid.

It was of interest to determine the effect that the volume of lithium had upon the observed counting rate. The following experiment indicated the magnitude of this effect. An aqueous solution (1.2 cc) containing iron-59 activity was put into a 1/2 in. OD steel capsule. This was counted. The solution in the capsule was then diluted by the addition of a known volume of water (0.4 cc) and the diluted solution was counted again. The dilutions and countings were repeated several times. The data indicated that the counting rate decreased by approximately 1% as the solution volume was increased from 1 to 2 cc. However, an increase in solution volume from 2 to 3 cc resulted in a 10% decrease in counting rate. As the solution volume increased, the amount of absorption of the gammas by the liquid was increased. However, such absorption cannot be an important factor since this would result in a regular decrease of counting rate with solution volume. The explanation for this must be that, when the solution level approaches the top of the well in the scintillation counter (corresponding to a volume of 2.2 cc), the counting geometry becomes poorer. It can be concluded that, for sample volumes less than 2 cc, the counting efficiency is essentially independent of sample size.

Colorimetric iron determinations were mainly used to relate the counting rate of a sample to its iron content. A Beckman DU spectrophotometer was used in these determinations. Iron, in the plating solution and in the swipes from the rotor and crucible surfaces, was analyzed by the O-phenanthroline method.[16]

Iron in lithium was determined by a modification of the bathophenanthroline method.[17] Lithium metal was dissolved in water and the resulting lithium hydroxide was titrated with 6M HCl. An additional 5 cc of 6M HCl was added and the solution evaporated to dryness. The residue was dissolved with water, hydroxylamine hydrochloride added and the pH adjusted to four. Bathophenanthroline reagent was then added and the colored iron complex was extracted with three portions of amyl alcohol. The amyl alcohol extract was made up to volume with ethanol and the

optical density of this solution at 533 millimicrons was measured and compared with known standards.

Iron determinations on the lithium used to fill the crucible gave values of 5 and 7 ppm of iron. A similar iron determination on the 27.5 hr lithium sample, from the solution rate run, showed 35 ppm Fe. If the value of 0.85 counts min-μg of iron is used (see section on plating techniques), the counting rate of the 27.5 hr sample corresponds to 40.0 ± 3.6 ppm Fe. Similarly, colorimetric analysis of a lithium sample taken at the end of the solution rate run was 29 ppm Fe while the radiochemical value was 23.3 ± 2.4 ppm Fe.

APPENDIX III

Self Diffusion of Iron

The quantity of iron dissolved by lithium was determined by measuring the iron-59 activity in the lithium. It was therefore essential that the specific activity of the dissolved iron be known. The specific activity of the iron that is electroplated on the inside of the crucible in which the lithium is heated can be readily controlled. However, during the course of the heating period, the specific activity of the plated iron may be decreased by interdiffusion with the inactive iron of the crucible. The plated layer of active iron should, therefore, be thick enough so that the activity at the surface of the plate remains essentially constant during the experiment.

A number of workers have studied the self-diffusion of iron. The diffusion coefficient of alpha iron increases with temperature to a maximum of about 10^{-10} cm^2/sec and then falls off very sharply at 1670°F to about 10^{-11} cm^2/sec, when gamma iron is formed. Values for the self-diffusion coefficient at 1600°F are in the range of 2.0×10^{-11} cm^2/sec.[18] Similarly, for iron at 1800°F, values for the self-diffusion coefficient are in the range of 8.1×10^{-13} to 2.6×10^{-12} cm^2/sec. It has also been observed[19] that if the iron is fine grained, the diffusion coefficient is greatly increased.

A few experiments were made to determine the effect of self-diffusion on a system similar to one used in the solution rate experiments. A 5-mil thick sheet of Swedish iron was electroplated on one side with radioactive iron, using a carbonate bath. On the surface area of 62 cm^2, 1.975 g of iron were deposited. This corresponds to a plate thickness of 4.05×10^{-3} cm (1.59 mils). The electroplated sheet was then annealed in a hydrogen furnace at 1600°F for 20 min.

The electroplated sheet was cut into tabs, 4.3 cm × 3.1 cm. The tabs were then heated in a furnace, through which argon gas was flowing, for varying periods at either 1600 or 1800°F.

After the heating period, an area of 2.0 cm × 1.0 cm on the electroplated surface of the tabs was electropolished. A mixture of 50 cc of perchloric acid solution (2 parts concentrated perchloric acid to one part of water) and 3 cc of 30% hydrogen peroxide was used as electropolishing solution. The samples were electropolished at about 2 amperes for 15 or 30 sec. The weight of iron electropolished was in the range of 7 to 18 milligrams corresponding to a thickness of 0.15 to 0.40 mils. The electropolishing solution was then evaporated to dryness. The residue was dissolved in a few drops of hydrochloric acid and this solution was counted. The counting time was 60 min and this resulted in counts above background in the range of 4000 to 7000 cpm.

The percent of the original activity that is expected in the electropolished layer has been computed using diffusion coefficients of 2.3×10^{-10} cm^2/sec at 1600°F and 3.1×10^{-11} cm^2/sec at 1800°F. This computation has also been made using Mehl's[3] values of 2.9×10^{-11} cm^2/sec at 1600°F and 8.1×10^{-13} cm^2/sec at 1300°F. The results are given in Table 2.

Table 2 — Self-Diffusion of Iron

Temperature, °F	Time, hr	Electropolished Layer Distance, mils from Surface	% of Activity Found in Electropolished Layer	% of Activity Expected in Electropolishing Layers: From Diffusion Coefficients Given in This Report	% of Activity Expected in Electropolishing Layers: From Mehl's Data
1600	4	0.21-0.50	91	85	100
	4	0.32-0.71	83	84	100
	23	0.28-0.75	57	48	87
	23	0.29-0.52	80	47	91
	24	0.00-0.35	43	48	90
1800	4	0-0.20	84	100	100
	4	0-0.16	98	100	100
	24	0-0.46	92	89	100
	24	0-0.47	87	89	100

At the moment there seems to be no obvious reason why the amount of diffusion observed in these experiments was so high. The literature values were obtained by a method which involves plating a very thin layer of active iron onto an inactive sheet of metal. The change of the amount of iron activity in the iron sheet was then measured. In the present experiments, a relatively thick plate of active iron was used. Self-diffusion of iron inside the electroplated layer is, therefore, important. The plated layer was fine grained and may have contained occluded impurities. It is therefore possible that the diffusion coefficients observed may be larger than those reported for large-grained high purity iron.

The total amount of iron-59 activity and the plating thickness required for the solution rate experiments can be derived as follows. It is desired that 1 microgram of iron, dissolved in a gram of lithium, give a net counting rate of 5 counts/min. For a 3.5% counting efficiency (experimentally determined for the counting technique used) this corresponds to 6.4×10^{-5} curies/gram of iron. The weight of a 1-mil plate on both the crucible and rotor was 17.1 grams. This corresponded to 1.1 millicuries per mil of plate.

It was required that the specific activity at the electroplated surface change by less than 10% during the course of an experiment. In this system the following equation was applicable:

$$C = C_0 \operatorname{erf} \frac{h}{2\sqrt{Dt}}$$

where C = concentration of Fe^{59} at distance x and time t
C_0 = concentration of Fe^{59} at t = 0, x = 0
h = thickness of electroplated layer
D = diffusion coefficient
erf = error function.

For t = 24 hr and $D = 10^{-10}$ cm^2/sec (highest value shown by Mehl's curve for diffusion in α iron region), we have h = 2.75 mils for $C = 0.9\ C_0$. If a value of 2.3×10^{-10} cm^2/sec is used for the diffusion coefficient, the required plating thickness is 4.1 mils.

The total activity in a 4-mil plate will therefore be 4 mils × 1.1 mc/mil = 4.4 millicuries.

The above treatment is valid for a quantitative plating procedure such as the carbonate bath. In the case of the chloride bath most of the activity remains in the bath. If a 4-mil plate with a specific activity of 6.4×10^{-5} curies/gram Fe is desired, it can be shown that about 12.8 millicuries of iron-59 are required.

REFERENCES

1. A. deS. Bransuras, Corrosion, 9(3):78 (1953).
2. J. McKee, NDA-40 (June 30, 1958). (Classified).
3. B. Minushkin, Determination of the Solution Rate of Metals in Lithium, NDA-44 (June 30, 1958).
4. E. E. Hoffman, ORNL-2674 (March 1959) (Classified).
5. E. E. Hoffman, D. H. Jansen, Lithium Symposium – Analytical Procedures and High-Temperature Corrosion, ORNL-CF57-10-6 (Jan. 20, 1958).
6. E. A. Moelwyn-Hughes, The Kinetics of Reactions in Solution, Chap. 12, Oxford University Press (1947).
7. A. G. Ward and J. W. Taylor, Solution Rate Studies with Liquid Metals, AERE M R 1866 (Feb. 23, 1956).
8. A. G. Ward and J. W. Taylor, Dynamic Solution-Rate Studies of Solids in Liquid Metals, AERE M R 2113 (Jan. 1957).
9. J. W. Taylor and A. G. Ward, Kinetic and Equilibrium Solubility Studies in the Iron-Bismuth System, AERE M R 2295 (July 1957).
10. J. A. R. Bennett and J. B. Lewis, Dissolution Rates of Solids in Mercury and Aqueous Liquids, AIChE Journal, 4(4):418 (1958).
11. J. M. Lommel and B. Chalmers, Th. Isothermal Transfer from Solid to Liquid in Metal Systems, Trans. Met. Soc., AIME, 2.5.499 (1959)
12. L. F. Epstein, Static and Dynamic Corrosion and Mass Transfer in Liquid Metal Systems, CEP Symposium Series 53:20 (1957).
13. W. Arbiter and S. Lazerus, Purification of Lithium by Vacuum Distillation, NDA-39 (June 14, 1957).
14. W. H. Armistead, Jr., Anal. Chem., 14.207 (1942).
15. "Metal Finishing Handbook," p. 354, Finishing Publications, Inc. (1958).
16. E. B. Sandel, "Colorimetric Determination of Traces of Metals," p. 378, Vol. 3, Interscience Publishers, Inc., New York (1950).
17. G. F. Smith et al., Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies, Analyst, 77:418 (1952).
18. A. A. Zhoukhovitzky J. of Appl. Radiation and Isotopes, 5:159 (1959).
19. C. Berchevet and R. F. Mehl, J. Metals, 188:144 (1950).